



Noncovalent Modification of Carbon Nanofibers Using 2-Naphthalenethiol for Catalyst Supports in PEM Fuel Cells

Hyung-Suk Oh and Hansung Kim[†]

Dept. of Chemical and Biomolecular Engineering, Yonsei University 262 Seongsanno, Seodaemun-gu, Seoul 120-749, Korea

ABSTRACT :

A new synthesis method for the preparation of Pt electrocatalysts on carbon nanofibers (CNFs) is reported. In this method, Pt electrocatalysts are loaded onto 2-naphthalenethiol (NT) functionalized CNFs. The noncovalent functionalization of CNFs by NT is the effective way for better distribution of Pt particles and higher electrocatalytic activity in polymer electrolyte membrane fuel cells. It was found that the presence of NT acts as a poison to catalysts. Therefore, it is necessary to remove NT through the heat treatment at 400°C.

Keywords : 2-naphthalenethiol, Graphitized carbon, Non-covalent functionalization, PEM fuel cell

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1. Introduction

Carbon black (CB) is the typical catalyst support material for polymer electrolyte membrane (PEM) fuel cells. However, the intrinsic drawback in use of CB as catalyst support is electrochemical carbon corrosion. Many studies reported that electrochemical carbon corrosion occurring during fuel cell start-up and shut-down process is one of the major contributors to performance degradation of PEM fuel cells.¹⁻³⁾ Thus, the reduction in carbon corrosion is essential to increase the overall life time of fuel cells. To alleviate this problem, substantial efforts have been devoted to find corrosion resistant catalyst supports. Among various alternatives, graphitized carbon types such as carbon nanofibers (CNFs), carbon nanotubes (CNTs) and carbon nanocages (CNCs) have been studied extensively due to their high corrosion resistance.⁴⁻⁸⁾

In use of graphitized carbon as catalyst supports, however, it is difficult to load Pt particles on these supports effectively. The hydrophobic nature of their surfaces hinders dispersion in a polar solvent and pre-

vents a uniform distribution of Pt particles on the carbon supports. Thus, the surface of graphitized carbon has to be functionalized prior to their applications as catalyst supports in order to control their hydrophobic properties. The most common functionalization method is to chemically treat carbons in HNO₃ or H₂SO₄/HNO₃ acid solutions. The acidic treatment generates oxygen-containing functional groups on the carbon surface, which converts the surface of carbon to hydrophilic property.⁹⁾ This effect contributes to improvements in Pt loading and the distribution of Pt particles on carbon supports. However, our previous study revealed that such chemical oxidation method increases a large number of defects by introducing oxygen functional groups on the surfaces, resulting in an increase in the electrochemical carbon corrosion.¹⁰⁾

As an alternative functionalization method, a noncovalent functionalization of graphitized carbons via π - π interaction has attracted particular interest recently because it can functionalize the surface of graphitized carbon with preserving the intrinsic properties of graphitized carbon. Li et al loaded CdS and Pt nanoparticles on CNTs functionalized by 1-aminopyrene (1-AP).¹¹⁾ The surface of CNT becomes weakly positively charged due to the amino groups of 1-AP. This leads

[†]Corresponding author. Tel.: +82-2-2123-5753

E-mail address: elchem@yonsei.ac.kr

to the self-assembly of the negatively charged Pt precursors uniformly on the surface of CNTs. Benzyl mercaptan was also used to functionalize the surface of CNT.¹²⁾ The thiol group in benzyl mercaptan is intended to react with the Pt particle through the formation of a S-Pt bond leading to the uniform dispersion of Pt nanoparticles on CNT surface. However, the materials introduced to functionalize the graphitized carbon are remained after Pt particles are loaded on the carbon supports and its effect on the performance of electrocatalyst is not examined thoroughly. In this work, a novel noncovalent functionalization agent of 2-naphthalenethiol (NT) was introduced and the effect of NT modification on the electrochemical performance was examined.

2. Experimental Section

Surface modification of CNFs

CNFs were purchased from Suntel Co. Ltd. (South Korea). The Platelet-type CNFs were added to ethanol containing 2-naphthalenethiol (NT). The mixture was ultrasonicated for 15 min and then mixed for 3 h at 25°C under vigorous stirring. After that, the mixture was diluted with double-distilled water, being filtered through a cellulose acetate membrane. The NT modified CNF was obtained, which was denoted by NT-CNF. The NT-CNF was dried in a convection oven at 50°C to remove the residual solvent.

Preparation of catalysts

Pt catalysts were loaded on carbon supports by the modified polyol process which is introduced in our previous work.¹³⁾ The prepared NT-CNFs were mixed with desired amount of PtCl₄ and NaOH in ethylene glycol to form 40 wt% of Pt on CNFs. The mixture was refluxed for 3 h at 160°C under vigorous stirring. The solution was allowed to cool down to room temperature and left for 12 h with continuous stirring. 0.1 M of H₂SO₄ was then added to the mixture and the pH of solution was adjusted to 3. The mixture was kept stirred for 24 h. The resulting carbon-supported Pt catalyst (Pt/NT-CNF) in the solution was then filtered and thoroughly washed with water and ethanol several times. This was dried in air for 1 h at 160°C and a mortar was used to grind the Pt/C catalyst to form a fine powder. The prepared Pt/NT-CNF was heat treated at 400°C in air to eliminate NT remained on the CNFs. The Pt/NT-CNF catalysts before and

after the heat treatment were denoted by Pt/NT-CNF-BH and Pt/NT-CNF-AH, respectively.

Preparation of membrane electrode assemblies (MEAs)

Commercial Pt/C catalyst (40 wt% Pt) from Johnson Matthey Co. was used for the anode, and the synthesized sample was used for the cathode catalyst. The catalyst ink were prepared by mixing the catalyst powder with 5 wt% Nafion ionomer and isopropanol ultrasonically and sprayed directly onto a Nafion 212 membrane. The geometric area is 5 cm² and the Pt loading is fixed at 0.4 mg of Pt/cm².

Electrochemical and physical analysis

Cyclic voltammogram (CV) was used to determine the effective active surface area of the Pt/CNF catalyst. The experiment was performed in 0.5 M H₂SO₄ saturated with nitrogen using a conventional three-electrode cell. A glassy carbon electrode with a thin film of prepared Pt/CNF catalyst was used as the working electrode while platinum wire and standard Hg/HgSO₄ electrode were used as counter and reference electrodes, respectively. Polarization curves were obtained at a cell temperature of 75°C under ambient pressure, with O₂ or air at the cathode and H₂ at the anode. Pt dispersion on CNFs was inspected with high resolution transmission electron microscopy (HR-TEM, JEM-30100 model). X-ray photoelectron spectroscopy (XPS) was also performed to investigate the ratio and the kinds of functional groups on carbon surface which are produced by surface modification process. ICP-AES analysis was carried out to estimate the Pt loading over the carbon support.

3. Results and Discussion

Fig. 1 illustrates the functionalization mechanisms of the CNF surface through the noncovalent π - π interaction. The noncovalent functionalization involves an irreversible adsorption of 2-naphthalenethiol (NT) onto the hydrophobic surfaces of CNFs (NT-CNF). NT is a bifunctional molecule with a naphthalenyl group and a thiol functional group. The naphthalenyl group, being highly aromatic in nature, is known to interact strongly with the basal plane of graphite via π - π interaction. The thiol groups at the end of the molecules interact with Pt catalysts to form S-Pt bond resulting in homogeneous distribution of catalysts.

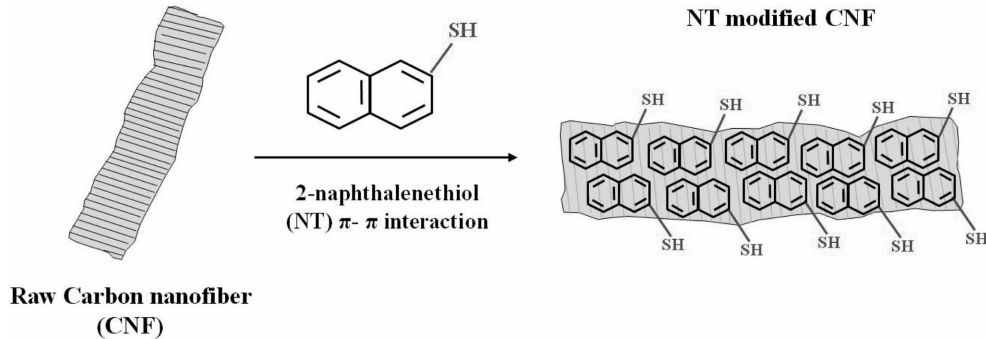


Fig. 1. Schematic diagram of the functionalization of CNFs with 2-naphthalenethiol (NT).

Fig. 2 shows HR-TEM images of the Pt particles on the NT modified CNF supports. For comparison, the Pt supported on the raw CNF (Pt/raw-CNF) was also included. In the case of Pt/raw-CNF, poor dispersion of Pt nanoparticles with a large number of aggregates was found (Fig. 2(a) and (c)). For the Pt/NT-CNF after heat treatment (Pt/NT-CNF-AH), the Pt nanoparticles are uniformly distributed on the CNFs with no agglomeration and are isolated with little interconnection (Fig. 2(b) and (d)). Smaller particle size and higher Pt dispersion on NT-CNF is attributed to the surface modification of CNF by forming a Pt-S bonding. According to ICP analysis, Pt/raw CNF gave the lower Pt loading of 18.8 wt% in comparison to

38.5 wt% for Pt/NT-CNF-AH. These results indicated that NT functionalization is helpful in increasing Pt loading and the yield of process. From the electrochemical surface area (ECSA) measurement by using CV, the ECSAs of Pt/NT-CNF-AH was $49.2 \text{ m}^2/\text{g}$, which is larger than that of Pt/raw-CNF ($41.1 \text{ m}^2/\text{g}$). This result implies that Pt nanoparticles on NT functionalized CNF are smaller in size and distributed evenly at higher Pt content. These results strongly support the benefit of NT functionalization of CNF for the particle size control and the increase in Pt content.

Fig. 3 shows the performance of PEM fuel cells prepared with the different cathode catalysts of Pt/raw-CNF and Pt/NT-CNF-AH. Polarization curves were measured at a cell temperature of 75°C with H_2 at anode and air at cathode with stoichiometry of 1.5

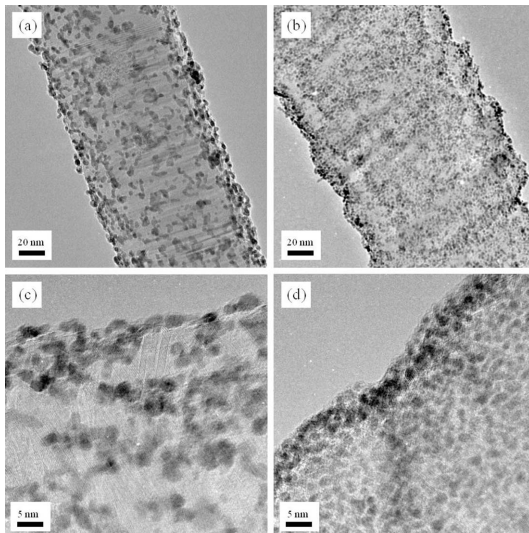


Fig. 2. HR-TEM images of Pt nanoparticles supported on raw-CNF (a, c) and NT modified CNF after heat treatment (Pt/NT-CNF-AH) (b, d).

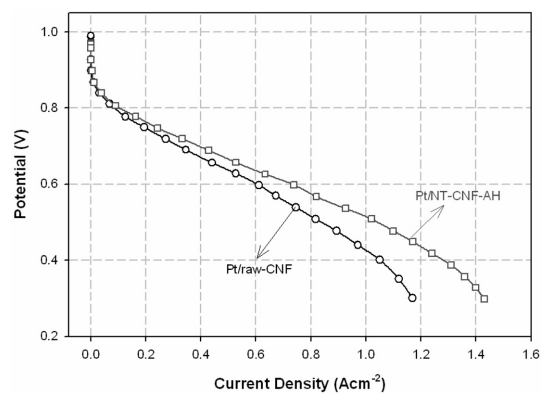
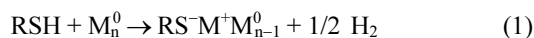


Fig. 3. Polarization curves for PEMFCs using the Pt/raw-CNF and Pt/NT-CNF-AH cathode electrocatalysts. Measurements were taken at 75°C with fully humidified reactants (the flow rates of 1.5 stoic H_2 and 2.0 stoic air). Pt loading was controlled at $0.4 \text{ mg}/\text{cm}^2$. No back pressure was applied during fuel cell operation.

and 2.0, respectively. At a cell potential of 0.6 V, the current densities for Pt/raw-CNF and Pt/NT-CNF-AH were 0.61 and 0.78 Acm^{-2} , respectively. The results suggest that the MEA prepared with raw-CNF showed lower performance compared to that using NT functionalized CNFs. This is attributed to the fact that Pt/raw-CNF has the larger platinum particle size and lower Pt mass content. The lower Pt mass content increases the thickness of the electrocatalyst layer in MEA resulting in increasing the transport resistance in the catalyst layer.

It is to note that the presence of NT is critical to the performance of MEA. Since sulfur bonded to Pt is known to behave as a catalyst poison,¹⁴⁾ heat treatment process was employed in the preparation of catalyst. In order to confirm the surface composition of Pt, XPS analysis was carried out and shown in Fig. 4. In general, the reaction between metal surface and thiol groups can be written as



which enables the change in the electronic state of metal surfaces and sulfur atoms.^{15,16)} It is therefore possible to detect the shift in binding energies from XPS analysis. Fig. 4(a) show that the Pt4f peak of Pt/NT-CNF before heat treatment (Pt/NT-CNF-BH) shifted toward a higher binding energy by 1.0 eV when compared with Pt/raw-CNF. The shift of binding energy is attributed to the ligand effect due to the interaction between Pt and sulfur in a thiol group. After the heat-treatment of Pt/NT-CNF (Pt/NT-CNF-AH) at 400°C, the Pt4f binding energy of Pt/NT-CNF-AH catalysts was restored to the initial state of Pt/raw-CNF. This implies that sulfur species originated from NT attached to the CNFs were removed away during the heat-treatment. This result is also confirmed by the fact that the sulfur peak was disappeared after the heat-treatment as shown in Fig. 4(b).

To examine changes in ECSA of Pt/NT-CNF, CV tests were performed before and after elimination of the thiol groups. For comparison, the Pt supported on the raw CNF (Pt/raw-CNF) was also included. As shown Fig 5, the effective surface area of the Pt nano particles was calculated from the area of the hydrogen desorption peaks between 0.03 and 0.3 V(SHE) after subtracting the contribution of the double layer charge. This area is converted into the effective active surface area of Pt using the conversion factor of 210 $\mu\text{C}/\text{cm}^2$. The effective surface area of the Pt/NT-CNF increases by 164.5% from 29.9 to 49.2 m^2/g after the heat-

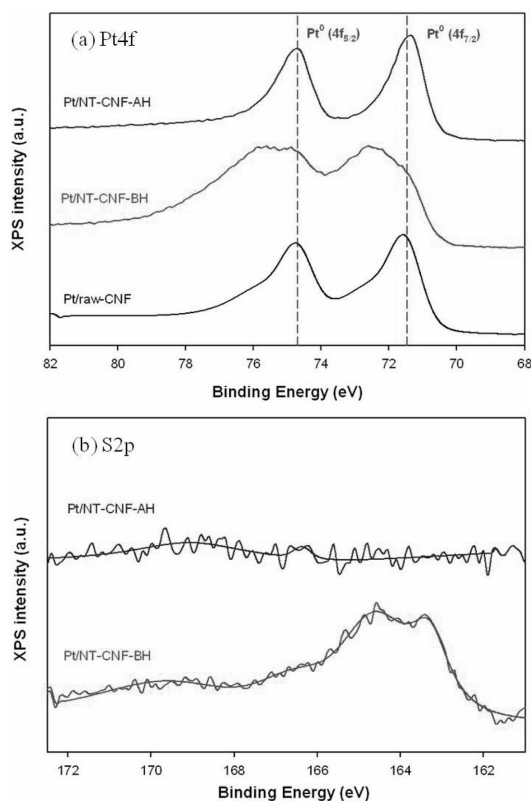


Fig. 4. X-ray photoelectron (a) Pt4f and (b) S2p spectra of Pt/raw-CNF and Pt/NT-CNF before (Pt/NT-CNF-BH) and after the heat treatment (Pt/NT-CNF-AH).

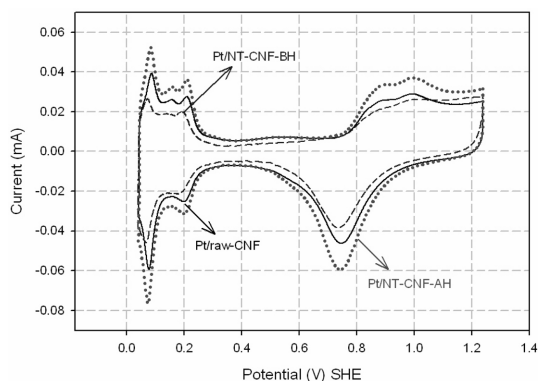


Fig. 5. The Cyclic voltammogram (CV) of Pt/raw-CNF, Pt/NT-CNF-BH and Pt/NT-CNF-AH. The electrochemical surface area (ECSA) was investigated under half-cell conditions using 0.5 M H_2SO_4 as the electrolyte. ECSA evaluated from the electric charge of hydrogen desorption wave in each CV.

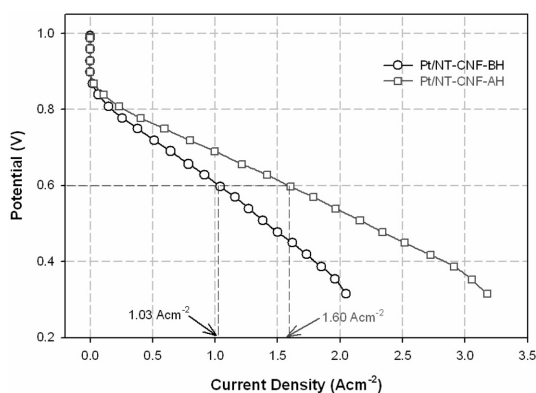


Fig. 6. MEA performance before and after heat-treatment of Pt/NT-CNF (Pt/NT-CNF-BH and Pt/NT-CNF-AH). Measurements were taken at 75°C with fully humidified reactants (the flow rates of 150 ccm H₂ and 150 ccm O₂). Pt loading was controlled at 0.4 mg/cm². No back pressure was applied during fuel cell operation.

treatment process. The performance of PEM fuel cells before and after the heat-treatment was shown in Fig. 6. The performance measured at 0.6 V increases tremendously from 1.06 A/cm² to 1.6 A/cm² after the heat treatment. These results indicate that the thiol functional groups of NT act as surface poisons in electrocatalytic reaction. The NT molecules should be eliminated from the surface of the resulting electrocatalysts in order to ensure high activity towards oxygen reduction reaction.

4. Conclusions

Graphitized carbon supports such as CNFs are functionalized by using 2-Naphthalenethiol (NT) successfully for better distribution of Pt particles and higher Pt content. NT forms a non-covalent bonding with a graphite surface via π - π interaction and the thiol groups at the end of molecules interact with Pt catalysts to form S-Pt bond. However, NT should be removed after Pt loading in order to avoid the deleterious effects

associated with catalyst poison. On the basis of the experimental results reported above, this NT functionalized method could be extended to the fabrication of various metals loaded graphitized-carbon supports.

Acknowledgments

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